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Research Laboratory

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Research Laboratory of the Eastman Kodak Company

THE PART that chemistry has played in the development of photography is aptly illustrated by a comparison of the crude, cumbersome apparatus which was necessary to make pictures years ago with the simple, compact, cameras and the stable and highly sensitive films available today. When a wet plate photographer started out for a day's picture-making with his pack of chemicals, plates, and dark tent on his back he resembled a prospector more than a camera man (Figure 1). Of necessity he was his own manufacturing plant. He chemically sensitized his own plates just before using, exposed them while wet, and developed them at once. Prints were made later on paper which he sensitized himself.

With the introduction of the dry plate and later the film, the crude methods of wet plate photography disappeared, the preparation of the materials became a commercial operation, and photographers now purchase almost all the materials that they use from firms who manufacture them in large quantities. This centralization has resulted in a far greater improvement in quality than would ever have been possible by individual effort.

Motion picture film was first sold in America in 1889 when George Eastman supplied narrow film "ribbon" to Thomas Edison. As now manufactured, it consists of a transparent, flexible base or support on which is coated a very thin layer of gelatin in which are suspended microscopic particles of a light sensitive silver salt. This upper sensitive layer is called the emulsion. To turn out millions of feet of film a year maintaining an unvarying uniformity of thickness, sensitiveness and quality requires a highly skilled organization backed by trained chemical research. In view of these conditions it would be quite impossible for an individual to prepare his own motion picture film.

Experimentation must also be always in progress to improve the film and to find new methods of manufacture. In all this work, chemistry plays an important part, not only

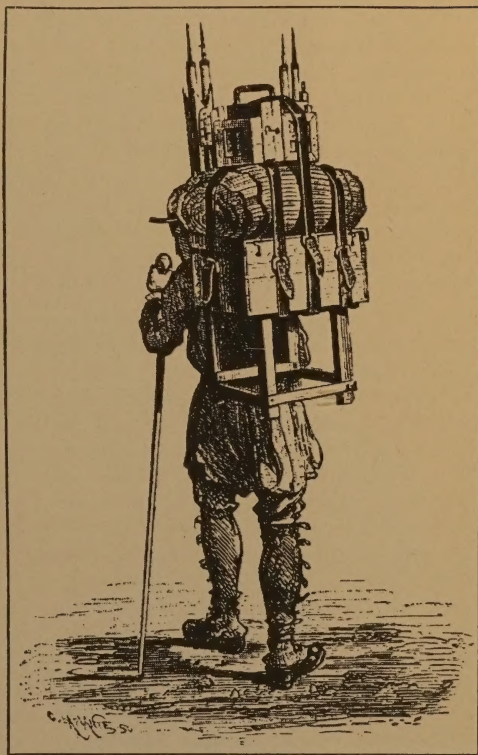


Figure 1—A Photographic Pioneer

in the manufacture and treatment but later in the processing, after treatment, tinting, toning, and renovating of the film. On the care with which these chemical operations are conducted depends the wearing quality or life of the film.

Chemistry in the Manufacture of Motion Picture Film

In the manufacture of motion picture films and other sensitized photographic materials, absolute cleanliness is very necessary at every stage of the process. All operations must be conducted in dust-free rooms and

only pure, clean, chemical substances are used.

Eastman motion picture film is manufactured at Kodak Park, at Rochester, New York. The plant consists of about 230 acres situated in the northwest section of the city. The output of this plant is roughly, 150,000 miles of film per year. To make this quantity, over five million pounds of cotton are used yearly, several millions of pounds of gelatin, and over twelve tons of solid silver per month.

The water necessary to take care of the needs in manufacture is pumped through a private pipe line into large reservoirs from Lake Ontario, 4 miles away. The reservoirs have constantly on hand sufficient water to supply a city of 150,000 people. The temperature of the workrooms is rigidly controlled at all times by refrigerating machinery, having a cooling capacity equivalent to the melting of 4,000 tons of ice every 24 hours.

In the preparation of film base or support, cotton is thoroughly washed in circular rotary vats with caustic soda solution to remove vegetable gums and other impurities. After carefully drying in huge dryers to eliminate all moisture (Figure 2), it is treated with two acids, nitric and sulphuric, a process known as nitration. Nitrating centrifugals, made of perforated baskets rotating inside a vat, are used for this process. The cleansed cotton is fed into the basket and the acids run in until the cotton is immersed (Figure 3). The fibrous structure of the cotton is not destroyed by nitrating but the treatment makes it possible to dissolve the cotton later in a solvent. When nitrating is completed the acids are drawn off and the basket rotated at high speed for draining. Nitrated cotton is known as cellulose nitrate. The excess acid is removed by placing the nitrated cotton in centrifugal washers. After washing in these machines, it is placed in large tanks of water where it is drained and rinsed repeatedly for several weeks. Centrifugal wringers operated at high speed next remove all the water. All these elaborate precautions are necessary in order that the cotton be freed from every trace of acid.

Washing and drying completed, the nitrated cotton is ready for dissolving in the organic solvents. These are usually compounds such as methyl alcohol to which certain other higher boiling liquids may be

added. The solvents are contained in large paddle mixers and the nitrated cotton is fed into them through chutes. When thoroughly mixed, the solution is a viscous liquid of the consistency of honey and is usually referred to as "dope." It is then piped to large air tight tanks until ready for coating (Figure 4). To remove any undissolved specks and fibres, the dope is filtered under great pressure. It is then coated on the surface of large polished wheels in a thin layer and as the wheels slowly rotate, the solvents evaporate, the film dries, and is peeled off. The thin sheets of transparent base 2,000 feet long, $3\frac{1}{2}$ feet wide, and approximately 5-1,000ths of an inch in thickness are wound up temporarily until ready to be coated with the emulsion.

For more pleasing presentation on the screen, motion pictures are often tinted by bathing the film in dye solutions which stain the gelatin. To save the finisher, the time and trouble of this operation, Eastman positive film is supplied in several different colors of tinted bases. In this product the color is impregnated in the film base.

For use in portable projectors which require a non-inflammable film, a special safety base called cellulose acetate is manufactured. It is made in much the same way as the nitrate except that acetic anhydride is used instead of nitric acid for treating the cotton so as to render it soluble in the organic solvents.

Preparing and Coating the Emulsion

We now turn to the making of the emulsion or the light sensitive layer that holds the photographic image. It is made in two grades, negative emulsion which is very sensitive to light and is used in the camera and positive emulsion which is much less light sensitive and is used for printing the pictures afterwards viewed on the screen. All emulsion making is conducted in rooms lighted with safelights which have been specially prepared for this purpose.

In negative emulsions the silver particles are about 8-100,000 to 12-100,000th of an inch in size whereas in positive emulsions they are less than 1-10 as large.

Silver, as used in making motion picture film, comes in bars each weighing about 42 pounds. (Figure 5). The bars are dissolved in nitric acid and after recrystallization in porcelain dishes pure crystals of silver nitrate are obtained. (Figure 6). Other in-

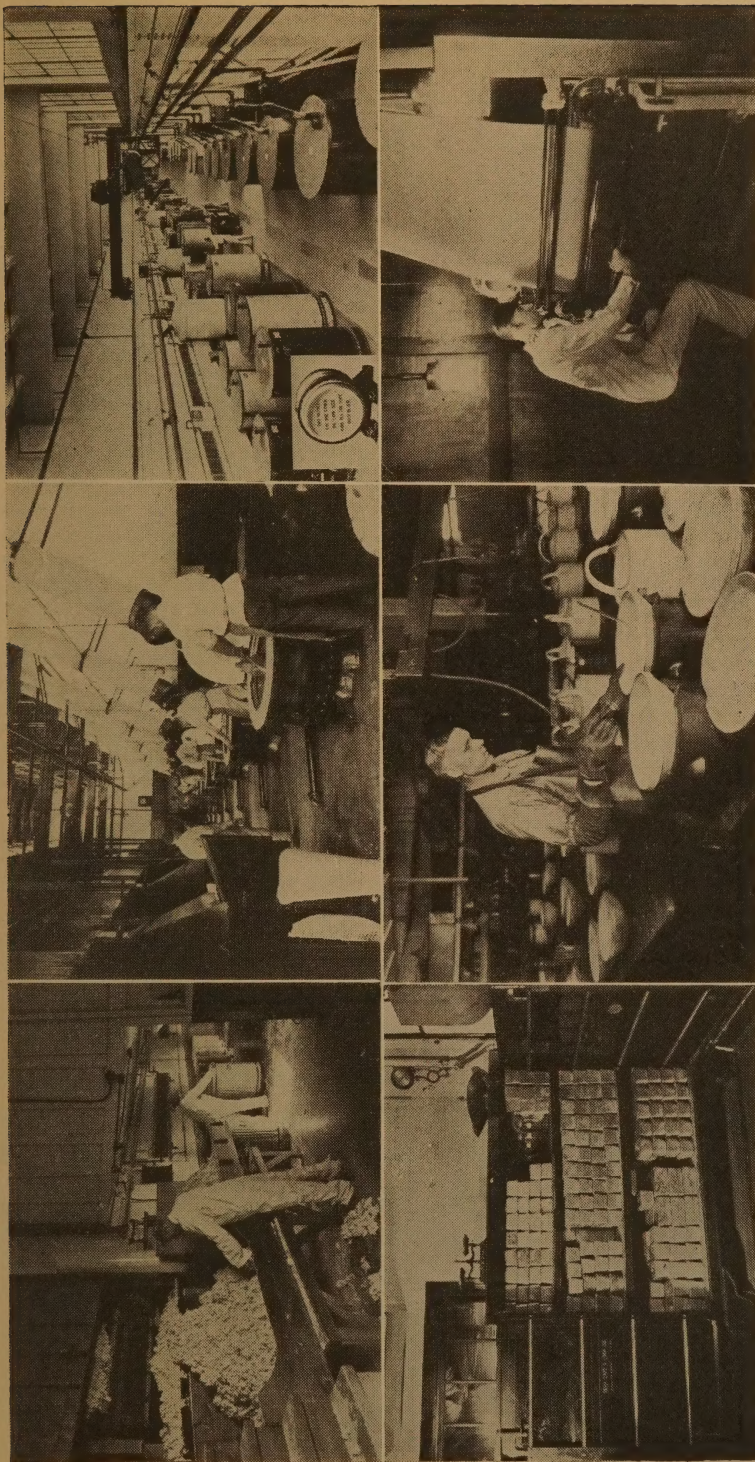


Figure 2 (top left) is the cotton dryer; figure 3 (top center) nitrating cotton; figure 4 (top right) "dope" storage tanks; figure 5 (lower left) bars of silver bullion; figure 6 (lower center) washing silver nitrate crystals; figure 7 (lower right) coating machine.

redients of the emulsion are potassium iodide, potassium bromide and gelatin. If these bromide and iodide salts are dissolved in water and to the solution thus prepared silver nitrate solution is added, an insoluble yellow salt is precipitated which is very sensitive to light, turning black after a few minutes exposure.

If this solution is coated on the base, the film would have very little sensitiveness and for all practical purposes it would be worthless. For this and other reasons the precipitation must be conducted in the presence of some material that will avoid these difficulties.

The material commonly employed is gelatin, a substance analagous to glue in composition, and like glue in that it is extracted from the bones and hides of cattle. Photographic gelatin is usually prepared from calf skin by soaking the skins in lime water, and subsequently extracting with hot water. The gelatin is dissolved in water and the bromide and iodide solutions carefully mixed with it. To this mixture heated to the correct temperature, is added the silver nitrate solution. The precipitate of the sensitive silver salt is held in suspension throughout the solution by the gelatin and because of this it receives the term, "emulsion."

These actual operations are conducted in silver lined steam jacketed vessels provided with usable agitators. Soluble salts formed during the reaction must be washed out of

the emulsion. This is accomplished by chilling it to a jelly, shredding it by pressing the mass through a chamber with a perforated bottom and sides, and washing the spaghetti-like strands many times with cold water. The shredded emulsion is then melted and coated.

For coating the emulsion on the base, special and delicate machinery is necessary in order to carefully control the thickness. The film base is handled in such a way that only one side comes in contact with the heated emulsion. (Figure 7). After the film is coated, it is carried in large loops through chilling rooms to set and harden or become "conditioned." When thoroughly dried, it is automatically cut into strips $1\frac{3}{4}$ inches wide and wound into rolls varying from 100 to 1,000 feet in length.

Perforating the film is carried on in a special department and the greatest care is required to have the work done accurately, for unless the perforations are correct in spacing, the film will not run smoothly in cameras, printers, or projectors and the picture will be unsteady on the screen. The rolls of perforated film are then taken to the packing room to be wrapped in selected pure black paper and packed in tin cans which are sealed to keep the contents air and light tight. The cans are stamped with the emulsion number, the footage, and are then placed in strawboard containers ready for shipment.

To make film of the high average quality demanded, inspection tests are necessary at

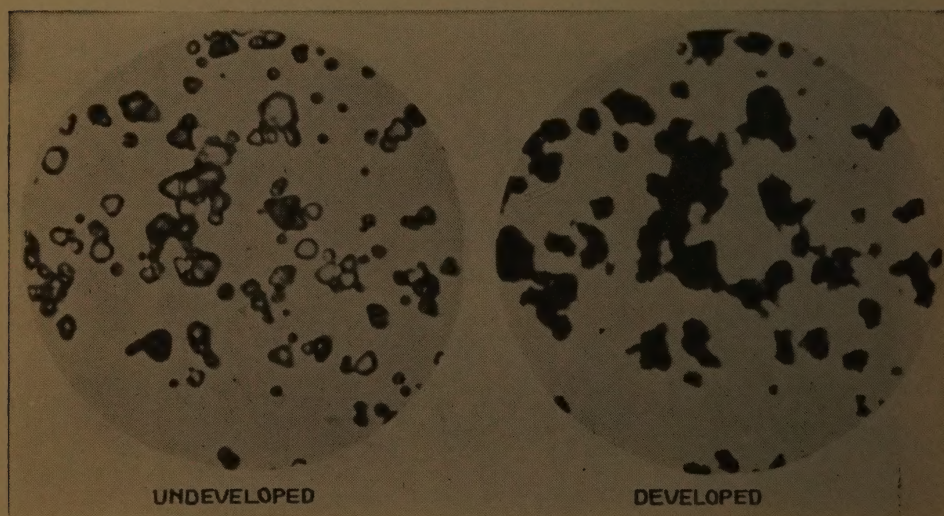


Figure 8—Every photographic image is composed of coke-like masses of silver grains—shown here under a powerful microscope.

every step in the manufacture. These include the actual making of pictures which are projected to show the photographic quality and to test the strength and wearing properties of the base. Thousands of feet of film are used up weekly in this way in a critical inspection of the manufactured product. No stock is permitted to reach the consumer which does not come up to the standard requirements.

Research on the Chemistry of Emulsions

In the manufacture of photographic emulsions, the art has preceded the science. Great refinements have been introduced in manufacture on a large scale but the real chemical causes and the factors controlling the reactions have until recently remained as much a mystery as in the early years when all emulsions were coated by hand. As a result of a large program of intensive research that has been in progress now for many years in the Eastman Research Laboratory and other laboratories, some of the uncertainty has been removed but much additional work remains to be done.

To gain a better understanding of this research work, something should be known of the actual characteristics of the emulsion. If a piece of exposed and developed motion picture film is examined under a high power microscope, the image will be found to be composed of minute grains or clumps of metallic silver, resembling tiny masses of coke. (Figure 8). These grains are derived from the original grains of the emulsion, which under the microscope are found to be crystals varying in shape from spheres to triangular or hexagonal plates in the larger grains. (Figure 9). They are of all sizes from very small grains to quite large ones and the properties of the photographic emulsion depend largely upon the various sizes which are present.

One part of this comprehensive plan of research has been the determination of the systematic relations which exist between the methods employed in the preparation of the emulsion and the photographic properties of the material obtained. That such relationships exist is now definitely established and before many years have passed a fairly complete understanding of these will have been arrived at.

One phase of this investigation has been the direct microscopic study of the grains in thousands of different samples of emulsions. This type of research is exceedingly tedious and progresses very slowly but it has proven one of the best lines of attack

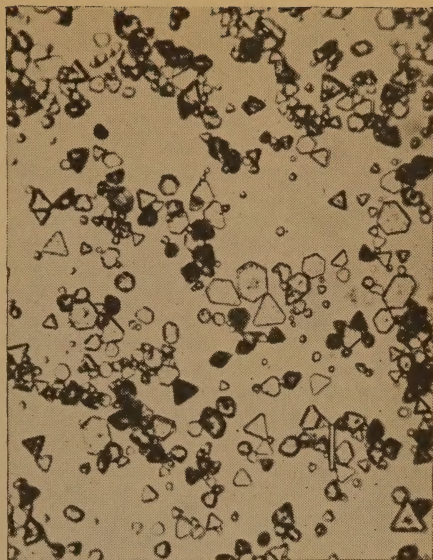


Figure 9—Silver Halide Grains of a Photographic Emulsion

on the problem. It will not be possible to fully describe the method but some idea of its complexity may be gained from the following statement. The emulsion sample is coated as a layer only one tiny grain in thickness by a scheme requiring a high degree of skill. A minute area of this layer is then photographed so as to enlarge it 10,000 diameters. The grains are next measured, classified according to size and from the results of hundreds of thousands of such measurements, a tentative conclusion may be drawn. This is essentially a statistical method of attacking the problem.

The chemistry of gelatin has also come in for a thorough study. That this is well worth while was forcibly proven by the recent discovery of a group of chemical substances which must be present in samples of gelatin even though in very small amounts in order that the gelatin be useful for making photographic emulsions.

These great problems of the chemistry of the preparation of the sensitive materials are only one part of the entire problem; the other is the use of the photographic materials. The faithfulness with which the final print reproduces the different tone gradations of the subject under various light conditions is known as the problem of tone reproduction. It may be reasonably said that this problem is fully solved and a statement of the accuracy of the reproduction of the tone gradations of any subject is now possible on any photographic material under any given condition of illumination.

Color Sensitivity of Motion Picture Films

When a beam of white light (usually sunlight) is passed through a prism it spreads out into a multi-colored band called the visible spectrum. The normal eye can distinguish several prominent hues in this spectrum, violet at one end, then blue, green, yellow, orange, and red. If this colored spectrum is photographed upon ordinary film, only the violet and blue would be completely recorded and the green very slightly while the yellow and red would have scarcely any effect at all. A red object therefore, which appears relatively bright to the eye photographs as black whereas blue and violet objects photograph as white. The result is a false reproduction of almost the entire range of color tones. The chemist was responsible for making photographic emulsions sensitive to colors. It was found that on adding certain dyes called sensitizing dyes the sensitiveness of the emulsion to green and yellow was increased. Such emulsions are called orthochromatic emulsions. Negative motion picture film is of this type but is relatively insensitive to red light and may be handled safely in darkrooms lighted with red safelights. It is manufactured in two speeds, par-speed and super-speed film; the latter being about twice as sensitive as the former. Within the past twenty years other sensitizing dyes have been discovered which on incorporation in emulsions made them sensitive to the entire spectrum. An

emulsion of this type is known as a panchromatic emulsion. (Figure 10). Natural color photography has been made possible by the chemist's discovery of these dye substances and their use in the manufacture of panchromatic film. Such pictures as Douglas Fairbank's "Black Pirate" could never have been produced without panchromatic film.

Color Filters for Absorption.—Although panchromatic motion picture film is strongly sensitive to red, yellow and green, it remains more sensitive to blue and violet especially when photographing by daylight. To correct for this extra sensitiveness to the blue and violet, color filters are used before the lens. These filters consist of thin sheets of dyed gelatin cemented between two pieces of optical glass. The dyes are carefully selected with reference to the portions of the spectrum which they transmit and absorb. For example, a yellow filter is most commonly used with panchromatic film since this filter absorbs a definite portion of the violet and blue light to which the emulsion is most sensitive thereby equalizing the exposure for all the colors. The result is a more accurate rendering of the tones of the subject.

When exposed to daylight or arc lamps, Eastman Panchromatic Negative Film is about equal in speed to Eastman Negative Film, regular speed. With tungsten lamps, it is considerably faster than standard speed Negative Film. Because of its excellent keeping qualities and its accurate rendering of tone values, panchromatic film is now being used extensively for both portraiture and landscape work.

Panchromatic film can be supersensitized by bathing for 1½ minutes in 4 percent ammonia at 50 degrees F., and drying as rapidly as possible. When given this treatment, the film is known as hypersensitized film and is about as fast as super speed negative film for daylight work (see Figure 10). It should be used as soon as possible after hypersensitizing but if necessary to store for a week or so, it should be kept dry and at a temperature not higher than 50 degrees F. The red and green sensitiveness of the film is increased three or four times by this hypersensitizing treatment which is a great advantage if exposures through red filters are to be made.

By the use of appropriate filters and treatment with certain sensitizing dye solutions, panchromatic film finds important applications for making "night scenes" in the daytime (Figure 11), and for making distant shots through haze. It may also be used for making duplicate negatives from posi-

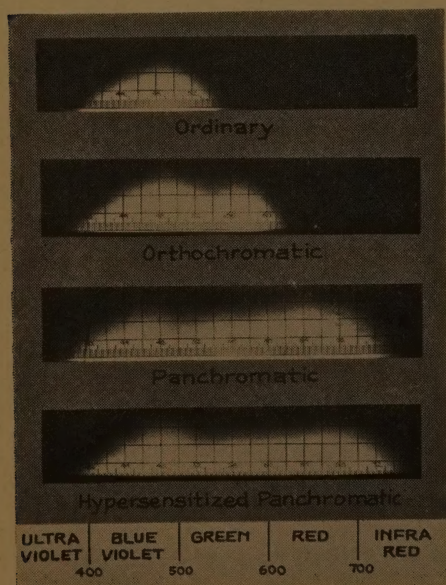


Figure 10—Spectrum photograph showing sensitivity range of several emulsions.

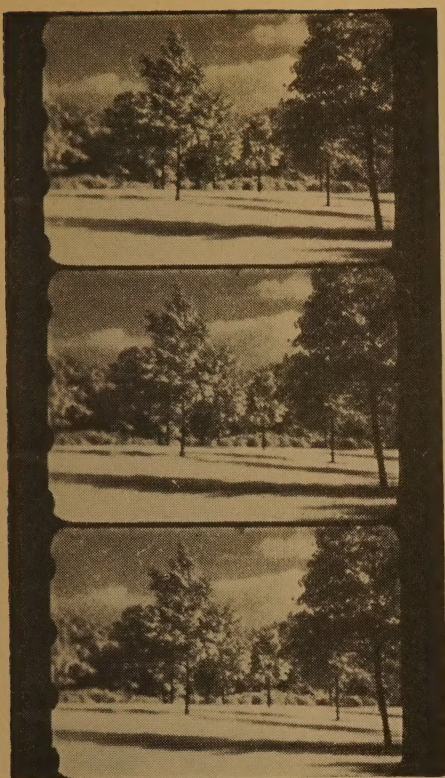


Figure 11—"Night scenes" photographed in daylight on specially sensitized film.

tives on tinted base when no other print is available. Colored spots and stains can be eliminated by duplicating in this way.

More complete information regarding panchromatic film is given in the booklet "Eastman Panchromatic Negative Film for Motion Pictures," supplied on application to the Motion Picture Film Department, Eastman Kodak Company, Rochester, N. Y.

Chemistry in the Processing of Motion Picture Film

After manufacture, motion picture film has little contact with chemistry until it has been exposed and is ready to be processed. The various treatments which it then receives such as development, rinsing, fixation, washing, and drying, are all chemical and determine in large measure the future permanency of the film. Besides the action of the different solutions in processing the film, there is considerable chemistry involved in the actual mixing of the solutions and in the action of the liquids on the vessels or tanks used for containing them.

Too little thought is usually given to the preparation of solutions used in photography.

We are apt to be satisfied to dump the chemicals into the water, stir the bath casually and proceed with the more important business of processing the film. Conversely, it is true, that it is unnecessary to take too great precautions and waste too much time in mixing the solutions, but more care should be exercised than is usually given.

Although distilled water or rain water are to be preferred for mixing solutions, experience has shown that it is only rarely that tap water which usually contains dissolved salts cannot be used. Providing the solution is filtered through a canvas cloth or allowed to settle before drawing off for use, very little trouble need be anticipated. The important thing is, however, to use only pure chemicals, dissolve each separately before adding the next, always mix them in the order recommended, agitate the entire volume of solution thoroughly as each constituent is poured in, and finally make up the solution to a definite volume with cold water. Hydrometer measurements are best avoided in mixing solutions (unless it is impossible to keep the chemicals dry), because it takes considerable time to adjust the strength of the solution. Hydrometer readings also vary with the temperature and no idea is conveyed as to the percentage strength.

A good arrangement for mixing the solutions is to place the chemical room directly above the developing room. Wax impregnated wooden tanks, enamelled vats or smoothly glazed earthenware crocks are recommended as containers connected with chemical lead piping to convey the solutions to the developing and fixing tanks in the room below.

Further details may be found by consulting the chapter on "Preparing Solutions" in the booklet, "Elementary Photographic Chemistry," published by Eastman Kodak Company. See also "The Development of Motion Picture Film" by J. I. Crabtree, Trans. Soc. M. P. Eng. No. 16, p. 163 (1922).

Developers and Development

The purpose of a developing solution is to change the exposed silver salt in the emulsion to metallic silver without affecting the unexposed silver salts. The constituent of the developer which accomplishes this change is called the reducing agent. The reducing agents now generally employed are elon, hydroquinone, pyro, and glycin. These substances are ineffective as developing agents until the solutions are made alkaline, usually with sodium carbonate, which activates the reducing agent. In the presence of the oxygen of the air, however, the reducing agent is oxidized and the solution turns brown. A

product somewhat like a dye is formed which stains the film and slows up the developing power of the solution. When the carbonate is added this rate of oxidation is increased, but if sodium bisulphite or sodium sulphite is added, the oxidation tendency is reduced and the solution turns brown very slowly. The sulphite, therefore, generally should be dissolved first as it acts as a preservative. Besides the reducing agent, the activator, and the preservative, the developer contains a restraining agent or potassium bromide which assists in controlling the rate of development and preventing developer fog.

The various reducing agents differ considerably in their rate of development: elon, for example, develops the image much more rapidly than hydroquinone, but on prolonged development they produce similar images (Figure 12). Both these developing agents are usually added to a developer because hydroquinone, when used alone, develops too slowly, especially at low temperatures. For negative development, when soft images are desired, the proportion of elon should preponderate, while in the case of a positive developer, when more contrast

is wanted, the hydroquinone should be in excess of the elon.

The difference between the density or blackness of the silver image of the lowest exposure and the highest exposure is a measure of the "density contrast" of the negative. This difference in density increases with time of development, the greatest change usually occurring in the first 5 or 7 minutes of development. Every picture is really a series of varying tones and the particular developer used, the time and temperature of development of both the negative and the positive print all influence the range of the density value of the tones.

If development is continued too long, a chemical reduction of the unexposed grains of the emulsion takes place which is commonly spoken of as "fog." It is never advisable to develop longer than one minute less than the fogging point, and it is therefore important to know the time required to produce visible fog with the type of film being used. Occasionally substances get in the developer which fog emulsions very rapidly. A serious trouble of this nature was traced to the presence of certain bacteria

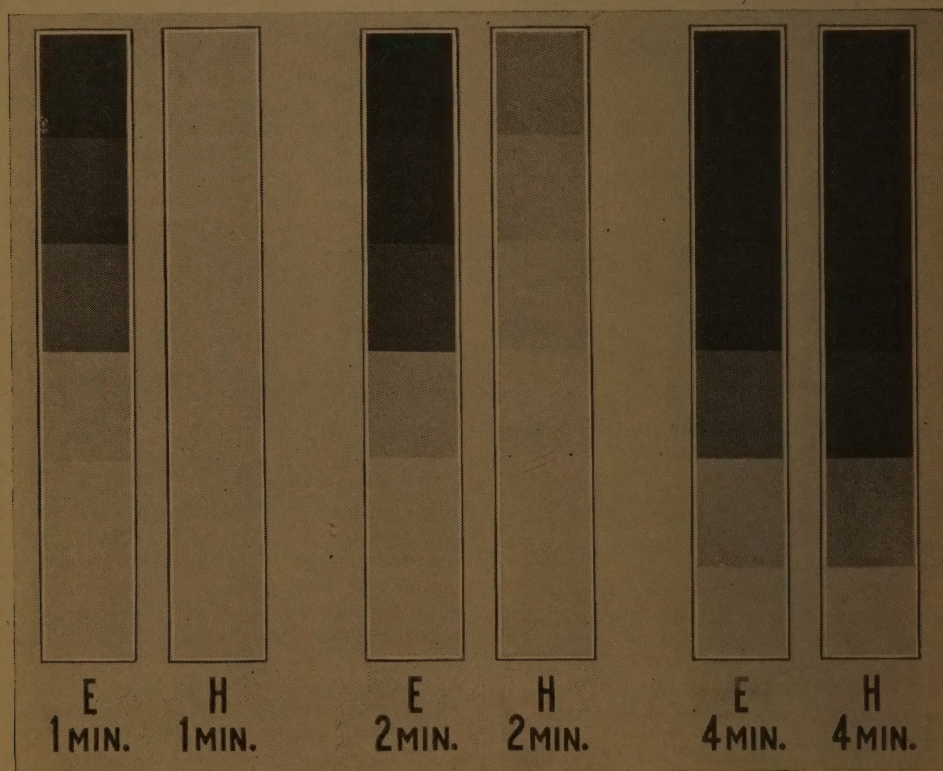


Figure 12—Graded strips showing comparative rates of development of (E) Elon and (H) Hydroquinone.

or fungi which acted on the sulphite in the developer, changing it to sodium sulphide, which fogs film very badly. Both the cause and a method of eliminating the trouble were worked out in the Eastman Research Laboratory in connection with an extensive investigation dealing with the classification of different types of chemical fog and the chemistry of developer solutions.

Effect of Temperature.—The properties of a developer solution are affected considerably by temperature, especially if there is much hydroquinone present. When the temperature is raised, development is faster and with a lowering of temperature, the development rate is retarded. The fogging point also changes with temperature. In warm weather developers do not keep as well because the higher temperature increases the rate of aerial oxidation. It is very important in view of these facts to know the temperature of the solution and to keep it fairly constant in order to duplicate results.

Tropical Procedures.—For handling and processing film under tropical conditions, a different technique is required. Standard methods have been worked out for insuring that the sensitiveness of the emulsion shall remain unimpaired and that the latent image be retained after exposure and before development. The secret of high temperature development is to prevent excessive swelling of the gelatin. The most successful method of doing this is to add an anti-swelling chemical such as sodium sulphate, or sodium phosphate to the developer and immerse the film in a hardening bath after development and before fixation. Such a hardening solution may be prepared with potassium chrome alum in 3 per cent. concentration, which works very well at temperatures from 75 to 85 degrees Fahrenheit. When higher temperature up to 95 degrees Fahrenheit are encountered, about 12 per cent. sodium sulphate should be added to this bath. Fixation can be conducted in the usual way after three minutes treatment of the film in this hardening solution. More complete data are given in a paper on "Handling Motion Picture Film at High Temperatures," by J. I. Crabtree, in the *Trans. Soc. M. P. Eng.* No. 19, p. 39 (1924).

Life of Developers.—The life or period of usefulness of a developer depends on its particular composition and whether it receives continuous or intermittent use. As a developer is used, the solution accumulates reaction products which tend to retard the rate of development, and it is, therefore,

necessary to develop for a longer time to secure a given contrast. Since reaction products slow down development, if a rack of film is allowed to remain stationary in a tank there is an accumulation of these by-products in the vicinity of the film which induces further retarding effects (Figure 13). Agitation of the rack and of the solution will prevent this trouble and give more uniform development.

With use a developer may become exhausted in several ways: (1) By aerial oxidation; (2) by accumulation of products resulting from the decomposition of the developing agents; and (3) by formation of sodium bromide and iodide from the reduction of these silver salts in the emulsion to metallic silver. An old developer may therefore have to be discarded because it develops too slowly or gives excessive stain or fog. When film is developed on a reel the solution is freely exposed to the air and if the developer does not contain an excess of preservative, chemical fog is produced. Experience has shown that the addition of about 5 per cent of old developer to a freshly mixed new developer will lower the tendency for chemical fog more than if the bromide concentration is increased above the normal quantity added. The chemical explanation of this effect is probably that the oxidized developer acts as an anti-fogging agent. Work is still in progress, however, to find the best method of reviving used developers.

For an extensive discussion of development, reference should be made to the paper, "The Development of Motion Picture Film by the Reel and Tank Systems," by J. I. Crabtree, *Trans. Soc. M. P. Eng.* No. 16, p. 163 (1922).

Developer Troubles.—Occasionally during processing, troubles arise caused by spots, marks, and stains appearing on the films. Methods of preventing, and removing many of these difficulties have been found and published, and data on others are being assembled and investigated.

Stains may result from using old developers containing an excess of oxidation products, from particles of chemical matter in the air of the room settling on the film, or from undissolved solid chemicals in the developer. They are sometimes produced by the formation of a scum on the surface of the developer due to insoluble oxidation products rising to the surface. Spots result from similar causes and in addition may be produced by bubbles of air clinging to the film on immersing in the developer or by splashes of oil which repel development. General stain may be the result of chemical fog or a



Figure 13—Streaks Caused by the Restraining Action of Products of Development.

coloring of the gelatin by an oxidized developing agent such as pyro. For full discussion of stains, see paper on this subject by J. I. Crabtree, *Amer. Ann. of Phot.* 1921, p. 204 or *Brit. J. Phot.* 68, 294 (1921).

When film is developed on racks in a tank, markings quite often occur at the points where the film passes over the top and bottom slats of the rack. These marks are caused by convection currents set up by the flowing away of chemical oxidation products as the development progresses. (Figure 14).

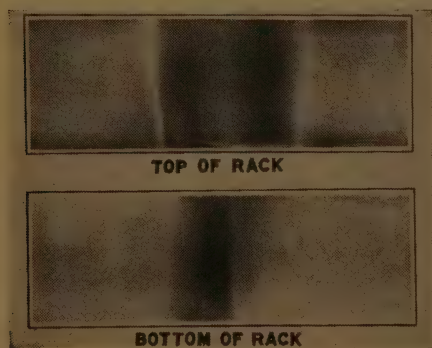


Figure 14—Rack Marks produced where film passes over slats of rack.

They may be very much diminished by agitation of the rack, by moving the film on the rack, or by the use of a special roller rack which permits easier movement of the film on the rack at intervals during the progress of development. (See paper on "Rack Marks and Air Bells," by J. I. Crabtree and C. E. Ives published in the *Trans. Soc. M. P. Eng.* No. 24 p. 95 (1926).

Chemistry of Fixation

A fixing bath contains as the active chemical agent sodium thiosulphate or hypo which dissolves the unexposed silver salts without affecting the silver image. A double salt of silver and sodium thiosulphate is formed which is very soluble in water and may be removed from the gelatin by washing. Hypo is seldom used as a plain solution but usually in conjunction with a weakly acid salt such as sodium bisulphite or with an acid hardening solution. The standard hardener contains a preservative, sodium sulphite which prevents decomposition of the hypo; an acid, usually acetic acid, to neutralize any alkali carried over in the film from the developer, thereby arresting development since an acid developer will not reduce silver salts; and a hardening agent, either potassium alum or chromium alum.

It is important to mix a fixing solution correctly. The hardener should be prepared separately by dissolving the sulphite first and when it is completely dissolved add the acetic acid. After the sulphite-acid solution has been thoroughly mixed, add the potassium alum. When the alum has dissolved make up to final volume with cold water and add the hardener solution slowly to the cold hypo while stirring the latter rapidly.

There are certain criteria used in judging the efficiency of a fixing bath as follows:

Rate of Fixation.—When film is immersed in a fixing bath, it is considered fixed when it has remained in the solution twice the time for the milky or opalescence of the unreduced silver salts to disappear. The

rate at which this takes place depends on the strength of the hypo (30% to 40% hypo fixes most rapidly), the emulsion used, that is whether negative or positive, the temperature of the solution (65° F. is recommended), and the degree of exhaustion of the solution.

Hardening Properties.—A certain minimum of alum is required to give the necessary hardening while an excess of alum may produce too much hardening and induce brittleness. Normal fixing baths are carefully compounded to give a hardening of 130° to 170° F., determined by immersing a strip of the fixed and washed film in water and heating the water slowly until the gelatin flows away from the support.

Sludging Tendency.—A fixing bath may become cloudy or precipitate a sludge in two different ways: (1) the hypo may break down giving a pale yellow sludge of sulphur which is the result of the temperature of the bath rising too high or of adding too much acid to the bath; and (2) the alum may be decomposed and a white sludge of aluminum sulphite formed which is the result of too low acidity, the presence of excess developer carried into the bath, or too high a sulphite concentration.

Effect of Temperature.—Changes in temperature of the fixing bath affect the rate of fixation and the life of the solution. If a film requires 95 seconds to clear at 65° F., for example, it would take about 50 seconds to clear at 85° F., but it is dangerous practice to allow the temperature of the bath to rise above 65° F., as the solution is apt to precipitate sulphur. Under tropical conditions where high temperatures and high humidities prevail, it is obviously often impossible to keep the temperature within this limit, and the fixing bath must usually be replaced oftener. A different technique must be used for tropical processing as mentioned previously under the subject of development.

Life of Fixing Solutions.—As a fixing bath is being used, the hypo becomes exhausted as a result of performing useful work in fixing out the emulsion. When the time for clearing negative film exceeds a certain point, say ten minutes, the bath should be discarded. The acidity of the bath is being reduced by the developer carried in although at first this tends to favor a longer sulphurization life. With continued use, however, the solution finally reaches a

point where a sludge of aluminum sulphite is precipitated rendering the bath useless. On the other hand, the hardening properties of a bath usually increase slightly during the first stages of use after which they fall off rapidly until the bath is revived.

Revival of Fixing Baths.—Since the acidity of a bath and its hardening properties are depleted before the hypo is used up, it is general practice to revive the bath at intervals by the addition of a definite quantity of acetic acid. When the acidity is lowered to two-thirds of the original value, enough acid should be added to restore the initial concentration. A fairly satisfactory method is to add acid after a certain footage of film has been passed through the solution. If the bath has formed a sludge before it was revived, the solution should be discarded.

Recovery of Silver.—An exhausted fixing bath contains dissolved silver salts and various methods have been tried to profitably recover the silver. The principal methods used are: (a) the sulphide method wherein sodium sulphide is added to the used bath and the silver is thrown down as a sludge of silver sulphide; (b) the hydrosulphite method in which the addition of sodium hydrosulphite precipitates a mixture of metallic silver and silver sulphide depending on the conditions of precipitation; (c) the zinc method which uses zinc in various forms, such as sheet, granulated, and dust; the silver being precipitated as metallic silver; (d) electrolytic methods which include the use of metallic units and the actual application of an electrical current. For recovery of large quantities of fixing bath, the sulphide method is most efficient; for medium quantities, the zinc dust method is satisfactory, and for small quantities, the use of an electrolytic recovery unit offers a simple and economical procedure.

Fixing Bath Troubles.—When the carbonate in the developer is neutralized by the acid in the fixing bath, carbon dioxide gas is formed which produces blisters which appear on the film as tiny craters providing the gelatin is too soft to withstand the disruptive action of the gas. If the bath has good hardening properties and the film is agitated on first immersion no trouble from blisters need be anticipated. If the fixing bath does not contain acid or if it is old and exhausted and contains an excess of dissolved silver, a chemical fog called dichroic fog is sometimes produced on the film. In reflected light, film fogged in this way looks yellowish green and by transmitted light it appears reddish pink. Dichroic fog never

occurs in a fresh acid fixing bath or if the film is rinsed before fixing and the temperature of the bath is kept at 65° to 70° F. When a partially exhausted fixing bath is allowed to stand several days without use, the hydrogen sulphide gas present in small quantities in the air reacts with the silver thiosulphate in the bath and forms a metallic-appearing scum on the surface of the solution. The scum consists of silver sulphide and should be removed by drawing the edge of a sheet of blotting paper across the surface of the bath. Trouble from sludging and precipitation has been discussed previously. Several different stains such as white aluminum sulphite stain, sulphur stains and yellow silver stains are occasionally produced. More complete discussion of fixing troubles is given in a paper on "Stains on Negatives and Prints," by J. I. Crabtree, Brit. J. Phot. 68, 294 (1921).

Chemistry of Washing

One might naturally think that there is little chemistry associated with washing film, and this is true so far as actual chemical changes are concerned, but it is a distinctly physico-chemical problem to determine the conditions that will ensure complete removal of hypo and other fixing bath components and oxidized products from the film. The nature of the water supply is not of vital importance, although if dirty water or sea water have to be used, the film should be subsequently given a thorough washing in fresh water.

The problem of washing film involves two principal operations: (1) separation of the chemical substances from the film, and (2) removal of these substances from the water in the vicinity of the film. Obviously the second operation must proceed equally as rapidly as the first, or the film would still retain some chemicals when taken from the wash water and stains would appear later. The first operation is really a problem of diffusion since the chemicals are held in the swollen gelatin layer and must find their way out to the surface. It has been found that as washing progresses under favorable conditions, the hypo content of the film is halved for each equal time interval. This "half period" value can be determined for each type of film. Most thorough washing results if the water is violently agitated at the point of contact with the film. Practically the ideal washing stream can only be realized by using a spray or an excessively large flow of water. Tanks should be as small as is consistent with the film output because the smaller the volume the more rapidly is

the stale water removed. To remove surface hypo, a few seconds rinse in a separate tank, or spraying with a coarse atomizer previous to the main washing is recommended. If it can be arranged, the cascade system is excellent. In this method, film is transferred successively through about five baths in which the water is circulating in a counter direction. In continuous tube processing machines, the water should be directed into the top of the last tube, flow from the bottom into the top of the next tube, and so on. A rinsing loop previous to the large washing tubes should be installed. Compressed air admitted at the bottom of a tank or tube provides the most economical and efficient method of agitation.

Washing Troubles.—If washing is incomplete as pointed out under the subject of fixation, trouble from stains and spots is often experienced. Sometimes these difficulties do not appear until several months or a year or two later, but the film is usually seriously if not permanently damaged. Several theories have been advanced to explain this deterioration, but it is most probable that the sulphur liberated from small traces of retained hypo in conjunction with bacterial action are the chief causes of the fading that take place through the formation of silver sulphide. Most trouble is experienced with film that has been poorly processed and stored in hot damp climates.

If the film is properly hardened no troubles will arise from having to wash in water whose temperature is 90° to 100° F. When film is thoroughly fixed and washed and subsequently stored at high temperatures, it rapidly becomes brittle and in a few years is completely destroyed by its own decomposition products. **It is very important, therefore, to store film when practicable at temperatures of 50° or 40° F.,** when the rate of decomposition is negligible providing, of course, that the proper care has been given the film during the processing operations. The motion picture industry is comparatively young, but there are samples of film in very good condition which were processed over thirty years ago. For more detailed information on the subject of washing motion picture film, see the article by K. C. D. Hickman, Trans. Soc. M. P. Eng. No. 23, p. 62 (1926).

When moisture comes in contact with dry film previous to or after exposure, or is deposited as the result of humid atmospheric conditions, or is left on the film previous to or during drying, certain characteristic

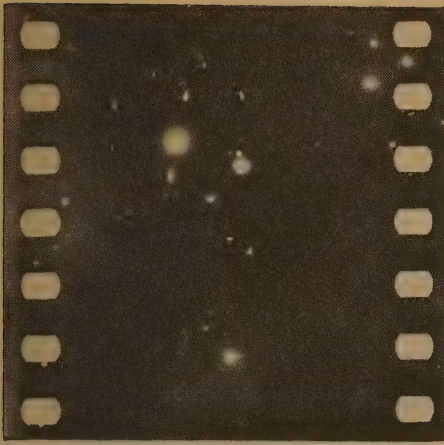


Figure 15—"Moisture Marks."

markings are produced. The most common example of these is a tiny white spot. (Figure 15). Various other types have been classified and several explanations advanced as to the causes and means of preventing such markings in a paper on the subject published in the *Trans. Soc. M. P. Eng.* No. 17, p. 29 (1923).

Corrosion and Its Relation to Construction Materials for Photographic Apparatus

In selecting a material for the construction of photographic processing apparatus, it is important to know the probable effect, if any, of both the material on the solution and the chemical action of the solution on the material. A metal like tin, for example, which is entirely satisfactory for pipe lines carrying distilled water, is on the other hand very unsuitable for use for constructing developer tanks as it reacts with the solution giving very bad fog. An investigation of this subject was made several years ago and the results published in a series of papers to which reference should be made for complete information. (See *Amer. Phot.* 18, 148, (1924)). A few of the conclusions may be of interest. Tin, copper, or alloys containing these metals should not come in contact with developers as serious trouble from fog will be experienced. Soldered joints in metal tanks are to be avoided. If metals must be used for apparatus to contain fixing baths, nickel, lead and monel are the only ones recommended, and these should be electro-welded or soldered from the outside except in the case of lead which should be burned. Aluminum, zinc, or galvanized iron should not be used with either

developers or fixing baths as these metals react with the solutions forming precipitates which deposit on the film and stain the gelatin.

Single metals or alloys are to be preferred to plated metals because when surface plating becomes worn or chipped they corrode very rapidly. Porous earthenware, fibrous materials, and rubber compositions should be avoided since the solutions crystallize out in the pores and subsequently disintegrate the material. Lacquered trays and japanned tanks are not suitable for containing strongly alkaline developers or acid fixing baths. Specific recommendations relative to the most suitable materials for constructing small apparatus, trays, tanks, tubes, troughs, piping, pumps, faucets, etc., are given in a paper on that subject which may be obtained on application to the Service Dept. Eastman Kodak Co., Rochester, N. Y.

Chemistry in the After Treatment of Motion Picture Film

Reduction.—Film is occasionally overexposed in the camera and although this can be partly compensated for in the printing, it is customary, to treat the film with solutions which chemically remove some of the image. This process is photographically termed "reduction" although it is not a chemical reduction but rather an oxidization since that portion of the image which is removed has been oxidized.

There are three general types of photographic reducers:

(1) Cutting reducers which remove the silver nearly equally from all parts of the image; (2) Flattening reducers which attack the heavy deposits more than the lighter areas; and (3) True scale reducers that attack both highlights and shadows proportionately. Reducers of the first type are; (a) Farmer's reducer consisting of potassium ferricyanide and hypo; and (b) the permanganate reducer which is a slightly acid solution of potassium permanganate. With Farmer's reducer, the silver is converted to silver ferrocyanide which the hypo dissolves. The permanganate reducer oxidizes the silver to silver sulphate which is sufficiently soluble in water to be dissolved. The net effect with either reducer is that the shadows of the negative are proportionately attacked the most, since they have less available silver to lose than the rest of image.

When a negative image has excessive contrast caused by overlighting or over development, a reducer of the second type is

necessary. An acidified solution of ammonium persulphate is the only solution known to act on the heavy silver deposits more than on the lighted ones. A fairly satisfactory explanation of the chemistry of this reaction has been reached and it is now known that silver sulphate is formed which dissolves in the solution.

When it is advantageous to reduce the printing time on a good negative, a true scale or proportionate reducer (type three) is sometimes employed. This solution consists of a compounded mixture of the permanganate and the persulphate reducers and it weakens the image in direct proportion to the amount of silver deposit present.

Intensification.—Although several methods have been worked out for chemically reducing the photographic image, it is quite another problem to add to or build up an image. As the saying goes, "what isn't there is hard to put there." A few solutions have been found, however, with which an underexposed or an underdeveloped image may be improved.

Usually intensification is performed by depositing a silver, mercury, or chromium compound upon the image. The most common mercury intensifier is Monckhoven's solution which uses a solution of mercury bichloride and potassium bromide for the bleach; this reacts with the silver forming a mixture of mercurous chloride and silver chloride. The image may be re-developed in several ways, with 10% sulphite solution, with an elon-hydroquinone developer, with 10% ammonia, and with a solution of potassium cyanide and silver nitrate, each solution giving proportionately greater intensification.

A chromium intensifier consists of an acidified solution of potassium bichromate which is used for the bleach. After a thorough washing, the image is redeveloped in a regular developer such as elon-hydroquinone. The chemistry of this intensifier is not very well understood but its use has found increasing favor owing to the ease and certainty of its operation and the permanency of the intensified image.

Tinting and Toning.—In order to obtain more pleasing effects on the screen, motion picture film is often colored by treatment with various chemical solutions. Tinting is accomplished by evenly staining the gelatin emulsion or the support by means of slightly acidified dye solutions. It is rarely neces-

sary to tint the emulsion since positive film on tinted support or base has been supplied for several years in nine different colors by the Eastman Kodak Company. This tinted positive film is printed and processed in the ordinary way. The use of tinted film thus eliminates several extra operations which are both expensive and troublesome.

Toning consists in changing the original silver image to a colored inorganic salt of silver or to a dye image. There are three commonly used methods of inorganic toning. In the first method known as sulphide toning the film is bleached in a ferricyanide-bromide bleach and subsequently treated with a weak solution of sodium sulphide which yields a final brown image composed of silver sulphide. Very beautiful blue tones are obtained by the use of a solution containing potassium ferricyanide and ferric alum in the presence of an alkaline salt of oxalic acid, a mineral acid and certain other salts. The silver image is thereby converted to a mixture of silver ferrocyanide and iron (ferric) ferrocyanide which forms the blue-toned image. Tones ranging from chocolate to reddish brown may be produced in a somewhat analogous way as the iron tones by the use of a bath containing uranium ferricyanide, the final image consisting of silver and uranium ferrocyanide.

If a silver image is converted more or less to a silver ferrocyanide image and the film immersed in a basic dye solution a mordanted dye image is produced. What happens is that the dye will attach or mordant itself to the silver ferrocyanide whereas it will not stick to the silver alone. This chemical reaction provides a method of obtaining a wide range of tones which may be still further extended by double toning. Basic dyes are the most suitable for use since they do not readily dye gelatin. Other effects may be produced by combining tinting and toning. For detailed information see the booklet, "Tinting and Toning Eastman Positive Motion Picture Film," published by Eastman Kodak Co.

Renovating Motion Picture Film.—After film has been projected and handled several times, it accumulates a certain amount of grease and dirt which detract from its projection value. If this is permitted to continue, the film may be badly damaged by scratching from grit. It is customary to renovate the film by treating it with solutions which will dissolve the grease and loosen the dirt. Gasoline, benzine, toluene, and xylene may be used for cleaning film but because of the inflammability of these chemicals, commercially pure carbon tetrachloride is preferable. All cleaning chemi-

cals or solvents must be used with discretion, however, and the liquid allowed to completely evaporate before the film is rewound, or the image may be subsequently attacked. Traces of sulphur chloride present in impure samples of tetrachloride probably cause fading due to deposition of sulphur which combines with the image forming silver sulphide. If pure tetrachloride is used and the film wound spirally on a drum, and the solvent applied with a soft cloth or velvet, the solvent will have sufficient time to evaporate before rewinding the film. Another non-inflammable solvent which does not fade the film is tetrachlor-ethylene. Similar precautions for cleaning on a large drum should be used. There are machines on the market in which the film passes over several moist felt pads saturated with solvents and then over a series of polishing wheels made with small pieces of velvet fastened around the periphery of the wheels. The polishing wheels rotate very rapidly and ensure thorough drying and polishing of the film before rewinding.

It is now usual practice to apply a narrow line of melted wax to new or first run prints along the center of the perforation area which provides against the liability of strain in first projection. Similarly when film is renovated it should always be rewaxed as the cleaning chemicals remove all or nearly all the wax.

Splicing and Varnishing Film.—Splicing of film is essentially a chemical problem since the film cement must possess certain properties, such as good adhesiveness, fairly rapid evaporation on drying, and have no corrosive action on the film support. When film has been projected many times it sometimes acquires scratches which fill up with dirt and grease and show up plainly on projection. Cleaning the film removes the dirt from the scratches but as soon as the film is put into use again the tiny grooves fill up as much as before. To prevent this, varnishes have been compounded for treating the film. Such varnishes have to be made very carefully as they must possess the same refractive index as film base or in other words the varnish layer must not change the direction of the light rays when the film is projected. Furthermore these varnishes must give a hard, non-abrasive surface when coated very thinly on the film and must not attack the support, the gelatin or the image.

Chemistry and Color Motion Pictures

A field which is demanding more attention yearly is that of natural color motion pictures. This problem is both an optical as well as chemical one; optically it demands unusual refinements in the design of lens systems and chemically it imposes a difficult problem in processing and in final dyeing of the films. There are two general classes of natural color motion pictures: those produced by additive and those by subtractive methods. These are further subdivided according as they use three color or two color ranges in color reproduction. In the additive process, several distinct color records are taken and projected separately and are either superimposed or shown in rapid succession, the colors being added to or built up on the screen. These processes usually require complicated and expensive apparatus. Whereas, in the subtractive method which has found most public favor the color records are taken separately but are finally incorporated on a single film and projected in the same way as standard pictures.

In the foregoing description of the value of chemistry in the motion picture industry, it has not been possible in view of the nature of this article and the diversity of the subject matter to discuss in much detail the actual chemistry involved. It is hoped that some idea may have been gained, however, of the importance of chemistry in every phase of the industry from the assembling of the raw material for manufacture to the final projection of the film.

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